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学位授与の題目	Low-temperature Deposition of Preferentially Oriented Polycrystalline Silicon Films and the Properties （高配向多結晶シリコン膜の低温堆積とその性質）
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学位論文要旨
Abstract

Polycrystalline silicon (poly-Si) has attracted extensive attention as an electronic material for integrated circuits, solar cells and thin-film transistors (TFTs) in liquid crystal display (LCD). The use of poly-Si, instead of amorphous silicon (a-Si) as an active layer for such electronic devices, has received much attention because the carrier mobility of poly-Si is much higher than that of a-Si. The presence of grain boundaries in the active region of poly-Si TFTs decreases the carrier mobility, limiting the device performance. On the other hand, the direct deposition of poly-Si at a temperature below the strain point of the glass substrates is an attractive and economical technology for producing the device quality silicon. The affection of the grain boundary can be generally reduced by growing uniaxially oriented poly-Si films and by increasing the grain size. In this thesis, in order to develop a method how to lower the deposition temperature along with growth of high-quality poly-Si films, we performed a systematic study focussed on the influence of structural properties of poly-Si with the assistance of various deposition parameters. The role of F- or H-related radicals on the crystallization were also discussed.

1. Introduction:

Poly-Si films were deposited by rf glow-discharge (at 13.56 MHz) decomposition using a SiH_4-SiF_4 mixture. The substrates were loaded horizontally on a quartz boat with its surface parallel to the axis of the reactor. The substrates were cleaned for 20 min by hydrogen and nitrogen plasma, respectively, just before the deposition of poly-Si films. The samples were deposited on 0.3-mm-thick glass (corning 7059) substrates with an area of 10×20 mm^2 for X-ray diffraction (XRD), Raman scattering and atomic force microscopy (AFM), 3×20 mm^2-thermally oxide Si for ESR and on single crystal Si (10^3 Ωcm) for FT/IR measurements. The control of T_d is an important factor dominating the crystallinity. In order to develop a method how to lower the deposition temperature along with growth of improved quality poly-Si films, the structure of poly-Si were investigated by varying deposition parameters. In the first stage of this investigations, the changes in the structural properties of poly-Si, deposited on a corning 7059 glass substrate at a low T_d of 400℃ (RF power of 20W, deposition pressure, P_d, of 0.25 Torr,) were investigated by varying the SiF_4 flow rate from 0 to 0.5 sccm under two different SiH_4 flow rates of 0.15 sccm and 1 sccm. In the second stage, we studied the structural change of poly-Si films deposited at 300℃ (RF power = 20W, P_d = 0.8 Torr, SiH_4 flow rate, [SiH_4] = 1 sccm and [SiF_4] = 0.5 sccm) caused by plasma pretreatments (under RF power = 90W) on the surface of glass (corning 7059) substrates, in which the substrates were exposed to H_2, N_2 and/or CF_4 plasma (for 20 min in each treatment) with different gas pressure. In the third stage, we investigated the effects of T_d (100-400℃) on the crystallinity of poly-Si, along with effects caused by changing [H_2] (= 0, 5 sccm) under [SiH_4] =1 sccm, [SiF_4] = 0.5 sccm, RF power = 20W, P_d = 0.25 Torr using SiH_4/SiF_4/H_2 mixtures.

2. Results and discussion

Figure 1 shows the crystalline volume fraction as a function SiF_4 flow rate ([SiF_4]) under two different SiH_4 flow rate ([SiH_4]) of 0.15 and 1 sccm. Crystalline volume fraction, ρ, was estimated from the intensity ratio of decomposed Raman spectra at around 480 cm^{-1} of amorphous component and around 520 cm^{-1} of crystalline component, respectively using an integrated Raman cross section for crystalline and amorphous phases. As shown in Fig. 1 when [SiF_4] increases from 0 to 0.5 sccm, it is found that the ρ values increase in good

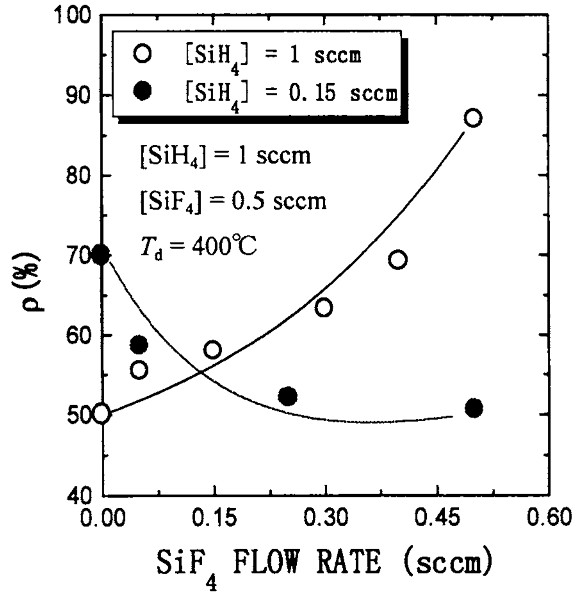

Fig. 1 Crystalline volume fraction (ρ), estimated from the Raman spectra as a function of [SiF_4] under [SiH_4] = 0.15 (closed circles) or 1 sccm (open circles).

correspondence to an increase in <110> grain size δ for [SiH_4] = 1 sccm. On the other hand, ρ values also found to decrease with decreasing both <111> and <110> δ for [SiH_4] = 0.15 sccm. The maximum ρ and δ values were found to be around 90% and 900 Å, respectively, for [SiH_4] = 1 sccm, and [SiF_4] = 0.5 sccm. These optimum values of feed gas flow rates were used as fixed conditions for the second and third stages of the work as discuss later, respectively.

Figures 2 (a) and 2 (b) show the values of δ obtained from the <110> XRD spectra and ρ as a function of plasma gas pressure, P_{PL} using different plasma species. In all poly-Si films used, no grains with textures other than the <110> orientation were found. As revealed in Figs. 2 (a) and 2 (b), when the substrates are subjected to successive treatments using N_2 and H_2 plasma (<N_2,H_2>) or to CF_4 plasma, the values of both <110>δ and ρ have their respective maximum values at nearly the same value of P_{PL} ($\approx$ 1 Torr), independent of the plasma species. In the estimation of δ, it was suggested that the relative error of δ for different films will be ± 15 nm using the Scherrer formula. So, we believe the presence of a maximum δ value at P_{PL} $\approx$ 1 Torr, though the error of the absolute value of δ may be rather larger. As shown in Fig. 2, the increase in δ is found to correspond well with the increase in ρ.

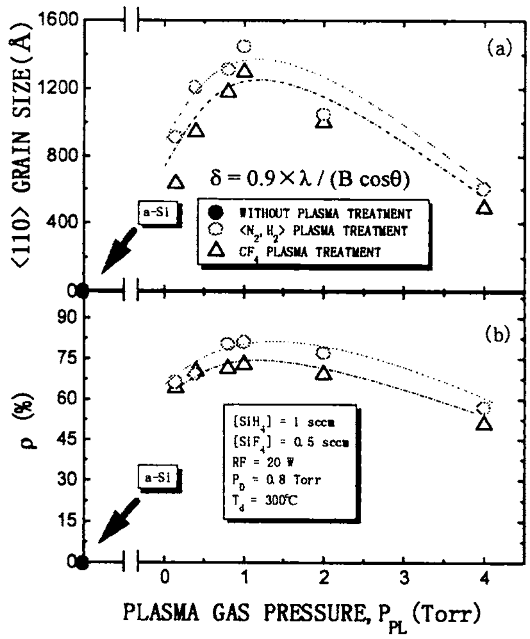

Fig. 2 (a) <110> grain size δ and (b) ρ as a function of plasma gas pressure, P_{PL}. The grain sizes, δ values were obtained using Scherrer formula inserted in Fig. 2(a). In this formula, λ is the wave length of the x-ray, B is the corrected half-width of the XRD spectra and θ is the angle satisfying Bragg's law.

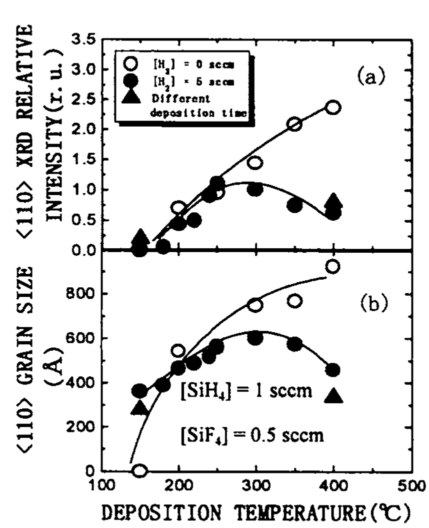

Fig. 3 (a) <110> XRD intensity and (b) <110> grain size, <110> δ for Si films deposited under conditions with and without hydrogen dilution, as a function of deposition temperature, T_d.

Figure 3 shows (a) the <110> XRD intensity and (b) the <110>δ for films with [H_2] = 0 and 5 sccm, as a function of T_d. In Fig. 3, the results denoted by closed triangles are those for the films with [H_2] = 5 sccm having different thickness. As seen in this Fig.3, the <110> XRD intensity and <110>δ value under the conditions of [H_2] = 0 sccm monotonically increase with increasing T_d. In addition, no crystallization in the film was found at T_d = 150℃, in contrast with the result for the film with $[H_2]$ = 5 sccm. Thus, under a relatively low T_d, the addition of hydrogen to the feed gases appears to improve the crystallinity. However, the addition of hydrogen at a high T_d is likely to deteriorate the crystallinity again.

3. Concluding summary

(1) An improvement in the crystallinity of PECVD poly-Si films (deposited at 400℃), due to the addition of SiF_4 to the SiH_4 feed gas, was interpreted by the effect of a change in the surface morphology of the substrates along with the effect of *in situ* chemical cleaning.

(2) PECVD Si films deposited on glass substrates without surface treatments were amorphous. However, when the substrates were exposed to <N_2,H_2> or CF_4 plasma with different P_{PL} values, the poly-Si films (deposited at 300℃) with a dominant <110> texture were grown and the most improved crystallinity was obtained at around P_{PL} = 1 Torr. The substrates then exhibited the smoothest surface. Such improved crystallinity was suggested to be caused by an increase in the grain size rather than that in the concentration of grains.

(3) At relatively low T_d (250-300℃), the addition of hydrogen gas to the feed gases improve the crystallinity of poly-Si. By contrast, the addition of hydrogen at a high T_d was likely to deteriorate the crystallinity again. Such changes in the crystalline quality caused by changing T_d and adding hydrogen were discussed in terms of the fluorine or hydrogen chemistry.

学位論文審査結果の要旨

各審査委員によって提出学位論文に関して個別に審査を行なうと共に，平成11年1月26日の口頭発表の結果を踏まえて，同日に論文審査委員会を開催して協議を行なった。その結果，以下のように判定した。

多結晶シリコン(poly-Si)の電子に対する易動度はアモルファスSiに比較してかなり大きいため，液晶ディスプレーにおける薄膜トランジスタ(TFT)や太陽電池用の半導体材料として大きな注目を受けている。このような目的においては，ガラス基板上にpoly-Si膜を堆積するため，ガラス基板の歪み温度より低い温度での堆積が不可欠となる。本論文は，ガラス基板の使用が可能となる，プラズマ化学気相成長(PECVD)法を使用してTFTや太陽電池用高品質poly-Si膜の低温膜成長技術の確立を目的としている。その技術手段として，(1)原料ガス中への，エッチングに対する活性度の大きなフッ素を含むSiF_4の添加量，(2)poly-Si膜の堆積直前におけるガラス基板のプラズマ処理の程度，(3)原料ガスへの水素の添加量，を変化させて結晶性を与える効果を調べている。結果として，原料ガス中にSiF_4および水素の両方を添加し，平滑な表面状態のガラス基板上にpoly-Si膜を堆積したとき，300℃以下の堆積温度の下で結晶化度が高くかつ強い〈110〉軸配向性を示すpoly-Si膜の堆積に成功している。

以上の研究成果は，基礎研究面のみでなく，前記したpoly-Si膜の応用目的の達成に対する重要な指針を与え，幅広い研究分野の発展に大きく寄与するものである。従って，本論文は，博士(学術)の学位に値するものと判断する。